ON THE ABSORPTION OF U.H.F. RADIO WAVES BY OPALESCENT BINARY LIQUID MIXTURES*

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ABSTRACT The absorption of ultra high frequency radio waves in two opalescent mixtures, *e.g.*, (1) nitrobenzene (50%)+hexane (50%) at 14°C and (2) aniline (46%)+cyclohexane (54%) at 34.5°C have been investigated in the frequency range 300–510 megacycles per sec. It has been observed that in each case a new absorption peak appears on the low-frequency side of the original peak observed in the case of one of the pure constituents having polar molecules. There is also another peak in the position of the original peak, but its height is much smaller than that in the pure liquid. It is concluded from these results that in the case of each of the two mixtures the polar molecules form two types of groups, in one of which the nature of packing of the molecules is identical with that in the pure liquid and in the other type the molecules are more closely packed.

The non-polar molecules of the solvent do not seem to be able to penetrate into these groups of polar molecules. It is pointed out that this method gives definite information regarding the change in the intermolecular field which takes place with the mixing up of polar molecules with non-polar molecules and furnishes definite information regarding the composition of the groups formed in opalescent mixtures.

INTRODUCTION

It was first shown by Krishnan (1935*a*) that the value of ρ_h observed in the case of the light scattered transversely by opalescent binary liquid mixtures is different from unity, although in the case of clear solutions the value is unity. This discrepancy was explained by Krishnan on the hypothesis that in the clear solution the scattering is due to single molecules whereas, in the opalescent mixture it is due to clusters of molecules. It was also assumed that the size of the cluster changes with the change of temperature of the opalescent mixture and at temperatures far away from the critical temperature, at which the mixture shows opalescence, the groups vanish. These light scattering data only show that there is local fluctuation in density in the mixture owing to the presence of small elementary volumes larger than single molecules and of such composition as produces heterogeneity in the elementary volumes. No information regarding the actual composition of elementary volumes or groups of molecules can, however, be obtained from the light-scattering data excepting the fact that the scattering is due to ellipsoidal particles of size not very small in comparison with the wavelength of light. It has, however, been shown recently by Sirkar and Sen (1949*a*) and also by Sen (1949) that the anomalous absorption

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of ultra high frequency radio waves observed by Drude (1897) and other workers is exhibited by many organic liquids and polar molecules if the temperature of the liquids is suitably adjusted and a suitable range of frequency of incident radio waves is chosen It is well known that applying Debye's theory, we can find out from the frequency of the absorption peak the viscous forces acting on the individual molecules. Since these forces are produced by the surrounding molecules, comparison of the position of the absorption peak observed in the case of the pure liquid with that observed in the case of the opalescent mixture gives us an idea of the change which takes place in the intermolecular forces on mixing the liquid with another liquid to form the binary mixture. This method is thus suitable for studying the nature of intermolecular field acting on the individual polar molecule in the opalescent binary mixture and is expected to furnish definite information regarding the composition of the groups of molecules which are responsible for the opalescene of the mixture It has, therefore, been decided to study the absorption of U.H.F. radio waves in a large number of opalescent binary liquid mixtures in order to find out the nature of the clusters of molecules formed in the mixture, and in the present paper results obtained in the case of two such mixtures have been discussed.

EXPERIMENTAL

The experimental arrangement used in the present investigation is the same as that described by Sen (1950). The mixture studied are nitrobenzene-hexane, and aniline-cyclohexane. In the former case the mixture contains equal weights of the two liquids and in the latter case it contains 46% by weight of aniline and 54% of cyclohexane The nitrobenzene-hexane mixture shows opalescence at 14°C while the other mixture is opalescent at 34.5°C. In the second case temperature of opalescence mentioned by Krishnan (1935*b*) is 30°C, but it was found that at 30°C the liquids quickly separate from each other, the heavier one settling at the bottom, whereas, at 34.5°C no such separation takes place Constant-temperature baths were used to keep these mixtures at the temperatures of opalescence. During the experiment, first, an empty bottle identical with that used to contain the mixture was placed between the oscillator and the detector and the reading in the detector at resonance was found with this empty bottle placed as the absorber. The bottle was then replaced by the bottle containing the opalescent mixture taken off from the constant-temperature bath. The detector was adjusted again for resonance and the reading was taken very quickly, so that the temperature of the mixture did not alter appreciably during this short period. This process was repeated for different frequencies of incident radio waves and also for the two opalescent mixtures. The absorption exhibited by pure nitrobenzene at 14°C, by pure aniline at 14°C and at 34°C and also by clear solution of nitrobenzene in hexane at 30°C was studied in this way in the frequency-range 300-510 mega cycles per sec.

RESULTS AND DISCUSSION

The values of the attenuation co efficient calculated from the ratio of the reading observed in the galvanometer in the detector circuit with the empty absorption cell as the absorber and that with the absorption cell filled with the mixture or the liquid, as the case may be, as the absorber are given in Tables I and II. In calculating the attenuation co-efficients in the case of the mixtures, a thickness equivalent to the proportion of the liquid in the mixture has been taken. The values have been plotted in figures 1 and 2 to show graphically the changes in the position of absorption peaks.

TABLE I

Nitrobenzene + *n*-hexane mixture

Frequency in Mc/sec.	Pure liq. at 14°C.		Mixture at 14°C		Mixture at 30°C	
	I_0/I	Atten. coeff.	I_0/I	Atten coeff.	I_0/I	Atten. coeff.
510	6.0	.461	1 82	.309	2 0	.357
505	6.66	.488	1.92	.336	1 875	.323
500	7 75	527	2 0	357	1.875	.323
490	6.0	461	1.90	.330	1 666	.263
480	3.42	316	1.70	.272	1 594	.240
470	2.64	.249	1.60	.242	1 575	.234
460	2 33	218	1.53	.219	1 562	.230
450	2 33	218	1.50	.209	1 534	.220
440	2.10	.191	1.50	.209	1.527	.217
430	2 20	.203	1 67	.262	1.517	.214
420	2.10	.190	1.605	.244	1.531	.219
410	1.76	.145	1.41	.177	1.526	.217
400	1.75	.144	1.36	.159	1.515	.214
390	1.73	.142	1.36	.159	1.458	.194

It can be seen from figure 1 that pure nitrobenzene exhibits a peak at about 497 megacycles per sec. at 14°C, while at 26°.7C this liquid shows a peak at about 505 Mc/sec (Sen, 1950[1]. The value of the attenuation co-efficient at the peak at the latter position is about 0.3 while this value increases to 0.53 at 14°C. In the case of the opalescent mixture at 14°C again, there is a peak at 497 megacycles per sec., but the height of this peak is much smaller than that observed in the case of the pure liquid at this

TABLE II

Aniline (46%) + cyclohexane mixture

Frequency in mc/sec	Pure liquid at 14°C		Pure liquid at 34°.5 C		Mixture at 31°.5 C	
	I_0/I	Atten. coeff	I_0/I	Atten. coeff.	I_0/I	Atten. coeff.
510	1 55	.112	1.45	.096	1 19	.096
505	1.58	.118	1.44	.093	1.12	.052
500	1 78	.148	1.42	.090	1.11	.056
490	1 50	.104	1.36	.080	1.09	048
480	1 36	.079	1.29	065	1.06	.035
470	1.30	.067	1.25	.057	1 07	.037
460	1 29	.065	1.25	.057	1.08	044
450	1.27	.061	1 23	.053	1.13	068
440	1.28	063	1.23	.053	1.10	.054
430	1 27	.061	1.22	.052	1.09	.046
420	1.27	.062	1.22	.052	1.08	.044
410	1 25	.057	1.21	.050	1 07	.037
400	1.24	055	1.21	.048	1.07	036
390	1 23	.052	1.20	.046	1 07	.037

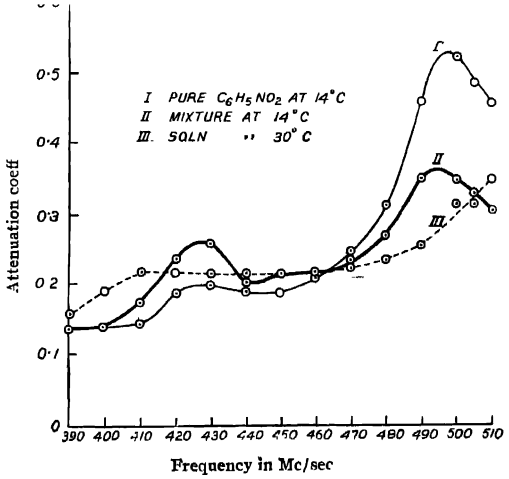

FIG. 1

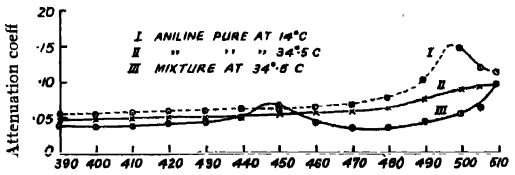

FIG. 2

temperature. Another new peak, however, appears in this case at about 427 megacycles per sec. In fact, pure nitrobenzene at 14°C also shows a very low hump at this position and this hump develops into a higher peak in the case of the opalescent mixture.

In the case of aniline at 34°.5 C there is hardly any absorption maximum in the range 300-510 megacycles per sec, but the absorption begins to increase monotonously at 480 megacycles per sec. and it seems that there may be a peak at a frequency much higher than 510 megacycles per sec. When the liquid is cooled down to 14°C an absorption peak at 498 megacycles per sec. is observed. In the case of the opalescent mixture at 34°.5 C, however a new peak at 447 megacycles per sec. is observed and the absorption begins to increase monotonously at 490 megacycles per sec. with the increase in the frequency of the radio waves.

The results mentioned above indicate that in both the opalescent mixtures, of the total number of polar molecules certain percentage has the same time of relaxation as that in the pure liquid at the same temperature, but a considerable proportion of the molecules has a time of relaxation larger than that of the molecules in the pure liquid. Since this time of relaxation is proportional to the product of the viscous force and the cube of the radius of the molecule, the observed increase in the time of relaxation may be due to an increase in either of these two factors If there would be association of molecules in these groups, the radius of the molecule would at least be doubled and in that case the increase in the time of relaxation would be very large, but the observed increase is too small to be accounted for in this way. Hence the viscous force acting on the molecule in these groups is larger than that acting in the pure liquid. It is to be inferred, therefore, that in the opalescent mixture there are groups of molecules in which the molecules are of the same species and in some of these groups they are packed exactly in the same way as in the pure liquid, whereas, in others they are more closely packed, so that the viscous forces acting on the individual molecule are larger in the latter case than in the former. The molecules in these groups are however, free to oscillate with the incident electromagnetic field.

It can be seen from figure 1 that the in the case of clear solution of nitrobenzene and hexane at 30°C, there is practically no absorption-maximum in

the range 390-510 megacycles per sec. The absorption increases a little at 410 megacycles per sec., remains almost constant over the range from 420-480 megacycles per sec and then increases rapidly at higher frequencies, showing that there is a peak at frequencies above 530 megacycles per sec. These results show that when the molecules of hexane intermix with those of nitrobenzene to produce a solution of uniform composition the time of relaxation of the nitrobenzene molecule diminishes appreciably and consequently the absorption peak shifts to higher frequencies. This shift again is not due to breaking up of associated groups of molecules in the solution, because in that case the shift would be much larger than what is actually observed. So the shift is due to diminution in the viscous forces. Thus it is clearly demonstrated that the study of the shift of absorption peak in this U. H. F. region gives us an idea about the change in the intermolecular forces in the mixture.

The arguments put forth above show that in opalescent mixtures, molecules of the constituent liquids do not mix with each other, but those of each liquid form very small elements of volume and such volumes disperse in the whole mixture in such a way that a heterogeneity in the density is created. The opalescence is produced by this heterogeneity.

Incidentally, it has to be pointed out that the absorption curves for the pure liquids at different temperatures obtained in the present investigation confirm the hypothesis put forward by Sirkar and Sen (1949*b*) that with the lowering of temperature the absorption peak becomes sharper and its height increases.

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